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## (54) COATING LIQUID FOR RESIST AND RESIST MATERIAL USING THAT

### (57)Abstract:

**PURPOSE:** To prevent the reduction of dimensional accuracy of pattern caused by interference between irradiating light and reflected light from the substrate in a photoresist film by incorporating a water-soluble film forming component and a fluorine-base surfactant.

**CONSTITUTION:** This resist coating liquid contains a water-soluble film forming component and a fluorine-base surfactant, and the resist material has a interference preventing film consisting of this coating liquid. In this case, the water-soluble film forming component is not limited as far as the component has solubility with water and has transmitting property for irradiating light. For example, this component has such properties that a uniform coating film can be formed by an usual coating means such as spin coating, no modified layer is formed between a film of this coating liquid and a photoresist film when the coating liquid is applied on the photoresist film, and further, a film having small absorption coefft. and high transmittance which sufficiently transmits active rays can be formed. The fluorine-base surfactant is not limited, and preferably an anion type nonmetal ion surfactant is used.

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**CLAIMS**

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[Claim(s)]

[Claim 1] Coating liquid for resists which contains a water-soluble film formation component and a fluoroochemical surfactant, and changes.

[Claim 2] The resist ingredient which has the interference prevention film which consists of the coating liquid for resists according to claim 1 on a front face.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

[Industrial Application] This invention relates to the resist ingredient using the new coating liquid for resists and new it. It is related with the resist ingredient which has the coating liquid for resists for forming the interference prevention film which can prevent lowering of the pattern dimensional accuracy resulting from interfering in this invention with the reflected light which exposure light has reflected from the substrate within the photoresist film in case a photolithography techniques perform pattern formation using a photoresist if it says in more detail on the resist film, and the interference prevention film which consists of this coating liquid on a front face.

**[0002]**

[Description of the Prior Art] In manufacture of a semiconductor device, after forming the photoresist film on substrates, such as a silicon wafer, and irradiating an activity beam of light selectively, a development is performed and the lithography technique of making the pattern of a photoresist forming on a substrate is used. And the thing of the negative mold with which dissolution clearance of the non-irradiated section of an activity beam of light is carried out as a photoresist, and the thing of the positive type with which dissolution clearance of the exposure section of an activity beam of light is carried out at reverse double in activity eye, and it is chosen suitably and used.

[0003] Moreover, that to which the semiconductor device manufacturing installation was also suitable for micro processing is examined and developed with the improvement in a degree of integration of a semiconductor device, for example, many aligners of an activity beam of light are also used in recent years from the cutback projection aligner using single wavelength, such as g line, i line, and an excimer laser, fitting micro processing.

[0004] By the way, photoresist thickness is received, in case the photoresist film is formed on a substrate and an activity beam of light is irradiated selectively at this. Changing pattern dimension width of face for interferential action is known, and it interferes in this interferential action with the reflected light which the exposure light of the single wavelength which carried out incidence to the photoresist film formed on the substrate has reflected from the substrate. For this reason, it originates in the amounts of light energies absorbed in the thickness direction of the photoresist film differing, and generates, the variation in the pattern dimension obtained after the variation in the thickness of the photoresist film developing negatives is affected, and pattern dimensional accuracy is made to fall as a result. The interferential action which especially lowering of such pattern dimensional accuracy became a big problem from the thickness of the photoresist film differing inevitably in the concavo-convex section of a level difference in case a detailed pattern is formed on the substrate which has a level difference, and was described above is lost, and development of the technique in which pattern dimensional accuracy is not reduced in the detailed pattern formed on the substrate which has a level difference is desired.

[0005] The approach of forming the antireflection film on a substrate and the approach of forming water-soluble-resin film, such as polyvinyl alcohol, as antireflection film on the photoresist film are proposed as a means to reduce such interferential action conventionally (JP,3-222409,A). However, the

former antireflection film is set to the approach of making it form on a substrate. To some extent, although interferential action can be reduced, if mask alignment is performed using the light of the same wavelength as exposure light, a mask alignment detecting signal will also become weak with the antireflection film on a substrate. After there is a fault that mask alignment is not made and precision improves a photoresist pattern a pattern imprint to an antireflection film, in order to have to remove without affecting a component It does not escape that the number of routings increases, but can necessarily apply to no substrate processings, and is not a practical approach. The actual condition be that development of the interference prevention film which could not respond to detailed-ization of the processing dimension in the semiconductor device manufacture field in recent years enough in that the approach of on the other hand form an antireflection film on the photoresist film do not have a complicated process since minute interferential action influenced pattern dimensional accuracy greatly in case the effectiveness of interference prevention be enough and a detailed pattern be form although it be practical, but be further excellent be demand strongly.

[0006]

[Problem(s) to be Solved by the Invention] This invention is the basis of such a situation and is made for the purpose of offering the coating liquid for resists for forming the interference prevention film which can prevent lowering of the pattern dimensional accuracy resulting from exposure light interfering with the reflected light from a substrate within the photoresist film on the resist film, in case especially a detailed pattern is formed, and the resist ingredient using this thing with a photolithography techniques.

[0007]

[Means for Solving the Problem] this invention persons came to complete this invention for the ability of that object to be attained based on a header and this knowledge with the resist ingredient which has the interference prevention film which consists of the coating liquid for resists containing a water-soluble film formation component and a specific surface active agent on a front face, as a result of repeating research wholeheartedly that the dimensional accuracy lowering based on interference of the light of a resist ingredient should be prevented.

[0008] That is, this invention offers the resist ingredient which has the interference prevention film which consists of the coating liquid for resists which contains a water-soluble film formation component and a fluorochemical surfactant, and changes, and this coating liquid on a front face.

[0009] About the water-soluble film formation component used for the coating liquid for resists of this invention Although there is especially no limit, for example that what is necessary is just what has water solubility and has permeability to exposure light with idiomatic spreading means, such as the (1) spin applying method Even if it carries out a paint film on (2) photoresist film which can form a uniform paint film, it is good to use what has the property of (3) activity beams of light which do not form a deterioration layer fully being penetrated between photoresist film, and being able to form a coat with high transparency with a small absorption coefficient in it.

[0010] As such a water-soluble film formation component, for example Hydroxypropylmethylcellulose phthalate, Hydroxypropyl-methylcellulose acetate phthalate, hydroxypropyl-methylcellulose acetate succinate, Hydroxypropyl-methylcellulose hexahydro phthalate, the hydroxypropyl methylcellulose, Hydroxypropylcellulose, hydroxyethyl cellulose, cellulose acetate hexahydro phthalate, Cellulose type polymers, such as a carboxymethyl cellulose, ethyl cellulose, and methyl cellulose, N and N-dimethyl acrylamide, N, and N-dimethylaminopropyl methacrylamide, N and N-dimethylaminopropyl acrylamide, N-methylacrylamide, Diacetone acrylamide, N, and N-dimethylaminoethyl methacrylate, Although vinyl system polymers, such as an acrylic polymer which makes a monomer N and N-diethylamino ethyl methacrylate, N, and N-dimethylamino ethyl acrylate, acryloyl morpholine, an acrylic acid, etc., polyvinyl alcohol, and a polyvinyl pyrrolidone, can be mentioned In these, the above-mentioned acrylic-acid system polymer, a polyvinyl pyrrolidone, etc. which do not have a hydroxyl group and which are a water-soluble polymer are suitable in a molecule, and especially a polyvinyl pyrrolidone can use it preferably. One sort of these water-soluble film formation components may be used, and they may be used combining two or more sorts.

[0011] On the other hand, although it can use without definition especially as a fluorochemical

surfactant, it is especially an anion type and the thing of a nonmetal ion system can use it suitably. By this anion type, as a fluorochemical surfactant of a nonmetal ion system The inside Rf of a general formula (I) RfCOOM and a general formula (II) R'fSO<sub>3</sub>M [type R'f is the hydrocarbon-group fluoride which replaced a part or all of a hydrocarbon group of a hydrogen atom by the fluorine atom. [ of the saturation of the carbon atomic numbers 2-20, or partial saturation ] M -- H -- NH -- four -- or -- N (R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>) -- it is -- R -- one -- R -- two -- R -- three -- R -- four -- respectively -- independently -- a hydrogen atom -- or -- low-grade -- an alkyl group -- being shown -- ] -- expressing -- having -- a fluorine -- an atom -- content -- a compound -- at least -- one -- a sort -- containing -- a thing -- it can mention -- As these fluorines atom content compound, a perfluoro caprylic acid, a perfluoro octyl sulfonic acid, perfluoro caprylic-acid ammonium, perfluoro caprylic-acid tetramethylammonium, etc. are mentioned, for example. Moreover, Fluorad FC-93 (3 M company make) marketed as a fluorochemical surfactant which contains perfluoroalkyl sulfonic-acid ammonium salt practical can use it suitably.

[0012] The coating liquid for resists of this invention is usually used in the form of a water solution, and, as for the content of a water-soluble film formation component, it is desirable that it is in 0.5 - 30% of the weight of the range, and, as for the content of a fluorochemical surfactant, it is desirable that it is in 0.5 - 50% of the weight of the range.

[0013] Moreover, the coating liquid for resists of this invention is usually used in the form of a water solution, as described above, but since the solubility of a fluorochemical surfactant will improve and membranous homogeneity will be improved if alcoholic system organic solvents, such as isopropyl alcohol, are contained, an alcoholic system organic solvent may be added if needed. In this case, the addition of this alcoholic system organic solvent is good to choose in the range to 20 % of the weight based on the coating liquid whole quantity.

[0014] Furthermore, to the coating liquid for resists of this invention, the various additives for raising a spreading film property can also be added according to a request in the range in which the object of this invention is not spoiled.

[0015] Although the resist ingredient of this invention has the interference prevention film which changes from said coating liquid to the front face Although there is especially no limit and it is usually used about the photoresist used for this resist ingredient, and it can be chosen out of inside as arbitration and the thing of a positive type, the thing of a negative mold, or the thing of a chemistry magnification mold can also be used without definition What consists of the photosensitive matter and a coat morphogenetic substance, and can be developed with an alkali water solution as a desirable thing can be mentioned.

[0016] Especially an advantageous resist is a positive type and a negative-mold photoresist equipped with many demand characteristics which may be adapted for the latest micro-machining enough. What consists of the constituent which contains the quinone diazide system photosensitivity matter and a coat morphogenetic substance especially as a positive type photoresist is suitable.

[0017] As said photosensitive matter, a quinone diazide radical content compound, for example, alt.benzoquinone azide, The compound which has the sulfonic acid, phenolic hydroxyl group, or amino groups of quinone diazide, such as alt.naphthoquinonediazide and alt.anthraquinone diazido, a part or full esterification, or as a compound which a part or the thing which carried out full amidation is mentioned, and has an aforementioned phenolic hydroxyl group or the aforementioned amino group For example, a 2, 3, 4-trihydroxy benzophenone, 2, 3 and 4, and 4'-tetra-hydroxy benzophenone, Polyhydroxy benzophenones, such as a 2, 2', 4, and 4'-tetra-hydroxy benzophenone, Or gallic-acid aryl, a phenol, p-methoxy phenol, Dimethylphenol, a hydroquinone, bisphenol A, a naphthol, A pyrocatechol, pyrogallol, the pyrogallol monomethyl ether, pyrogallol-1, 3-wood ether, a gallic acid, the gallic acid etherified [ which were etherified and was remnants-esterified ] in a part of hydroxyl group, an aniline, p-amino diphenylamine, etc. are mentioned. And especially a desirable quinone diazide radical content compound has desirable above-mentioned full esterification object and above-mentioned partial esterification object with polyhydroxy benzophenone, naphthoquinone-1 and 2-diazido-5-sulfonyl chloride or naphthoquinone-1, and 2-diazido-4-sulfonyl chloride.

[0018] Moreover, as a coat morphogenetic substance, alkali fusibility resin, such as a copolymer of the novolak resin, the acrylic resin, the styrene, and the acrylic acid which are obtained, for example from a phenol, cresol, a xylene, etc. and aldehydes, a polymer of hydroxystyrene, polyvinyl hydroxy benzoate, and polyvinyl hydroxy benzal, is effective. the weight average molecular weight which cut the low-molecular-weight region as a coat morphogenetic substance especially, using independent, or mixture and the novolak system resin compounded from aldehydes of cresol or a xylene as a desirable positive type photoresist -- 2000-20000 -- the thing of the range of 5000-15000 is preferably suitable.

[0019] 10 - 40 weight section and the thing preferably blended in the range of 15 - 30 weight section are preferably used for the photosensitive matter described above in said positive type photoresist to the coat morphogenetic substance 100 weight section.

[0020] Moreover, although there is especially no limit about a negative-mold photoresist and all things well-known as a negative-mold photoresist can be used conventionally, the negative-mold photoresist of the chemistry magnification mold which comes to contain three components of the binder used as a negative-mold photoresist for detailed pattern formation, an acid generator, and a base polymer is desirable.

[0021] Next, if one example is shown about creation and operation of the resist ingredient of this invention, after forming the photoresist film on substrates, such as a silicon wafer, the coating liquid for resists which is the above, and was made and prepared is applied on the photoresist film by the spinner method, by subsequently heat-treating, the interference prevention film is made to form on the photoresist film, and the resist ingredient of this invention is created. In this case, when obtained only by not required processing but the good paint film excellent in homogeneity applying, it is not necessarily necessary to perform heat-treatment. Then, after irradiating selectively activity beams of light, such as ultraviolet rays and far ultraviolet rays (an excimer laser is included), through the interference prevention film at the photoresist film using a cutback projection aligner, a resist pattern is formed on a silicon wafer by performing a development. This interference prevention film has the optimal thickness for reducing the interferential action of an activity beam of light effectively, and this optimal thickness is the  $\lambda/4n$  of odd times the formulas (inside of a formula: the wavelength of the activity beam of light which  $\lambda$  uses, and  $n$  show the refractive index of the interference prevention film). For example, if it is the interference prevention film of a refractive index 1.29, odd 48nm times are the optimal thickness [ as opposed to / to 85nm odd times and ultraviolet rays (i line) / to 71nm odd times and far ultraviolet rays (excimer laser) / an activity beam of light to ultraviolet rays (g line) ], respectively, and the range of double sign 5nm of each optimal thickness is desirable. Moreover, although this interference prevention film can also be removed to the development and coincidence of the photoresist film, in order to make it remove thoroughly, it is desirable to carry out exfoliation processing of the interference prevention film before a development. This exfoliation processing can remove only the interference prevention film thoroughly by applying the solvent which dissolves the interference prevention film, rotating a silicon wafer with a spinner. The water solution which blended the surfactant as a solvent from which the interference prevention film is removed can be used.

[0022]

[Effect of the Invention] In the manufacture field of the semiconductor device that dimensional accuracy does not fall in formation of the detailed pattern with which effectiveness sufficient in the conventional antireflection film was not acquired from the interference prevention film in the resist ingredient of this invention being able to form the resist pattern which was excellent in pattern dimensional accuracy as a result since it excelled in the operation which reduces the interferential action in a lithography technique, and a reduction operation of interferential action being excellent, the effectiveness which is extremely excellent in practicability does so.

[0023]

[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples.

[0024] On the 6 inch silicon wafer of 11 sheets, the rotational frequency was changed by the spinner method, respectively, THMR-iP3000 (TOKYO OHKA KOGYO CO., LTD. make) which is the positive

type photoresist which contains example 1 cresol novolak resin and a naphthoquinone diazido compound, and changes was applied, and photoresist thickness obtained the silicon wafer of the range which is 0.94-1.10 micrometers because 90 degrees C dries for 90 seconds on a hot plate.

[0025] Subsequently, on the photoresist film formed on the silicon wafer of 11 sheets In 24g of 10-% of the weight polyvinyl-pyrrolidone water solutions, it is fluorochemical surfactant FC-93 (to 73 % of the weight of water, and the solvent which consists of 27 % of the weight of isopropyl alcohol). After perfluoroalkyl sulfonic-acid ammonium salt blended 27g of the solutions and 3 M company make which were contained 26% of the weight, the coating liquid which added pure water and prepared the whole as 200g was applied, and 90 degrees C of interference prevention film of about 650A of thickness were formed by drying for 90 seconds. Then, after having performed 110 degrees C and BEKU processing for 90 seconds on the hot plate after exposing using cutback projection aligner NSR1755i7A (NIKON CORP. make), and carrying out a paddle development for 65 seconds at 23 degrees C with a tetramethylammonium hydroxide water solution 2.38% of the weight, the photoresist pattern was formed by washing for 30 seconds with pure water.

[0026] And when the graph which plotted dimension fluctuation of 0.45-micrometer line pattern on the axis of ordinate, plotted photoresist thickness on the axis of abscissa, and was obtained about the relation of the line pattern dimension of 0.45 micrometers and photoresist thickness which were formed with the same light exposure on the silicon wafer of 11 sheets, respectively was shown in drawing 1 , the maximum of dimension fluctuation was about 0.03 micrometers.

[0027] In the interference prevention film formation coating liquid used in the example of comparison 1 example 1, when the photoresist pattern was formed by the same actuation as an example 1 except not using a fluorochemical surfactant, it investigated about the relation between the line pattern dimension of 0.45 micrometers, and photoresist thickness similarly and the graph was shown in drawing 2 , the maximum of dimension fluctuation was about 0.10 micrometers.

[0028] On the 6 inch silicon wafer of nine sheets, the rotational frequency was changed by the spinner method, respectively, THMR-iN200 (TOKYO OHKA KOGYO CO., LTD. make) which is the negative-mold photoresist of the chemistry magnification mold which consists of three components of example 2 binder, an acid generator, and a base polymer was applied, and photoresist thickness obtained the silicon wafer of the range which is 0.93-1.03 micrometers because 90 degrees C dries for 90 seconds on a hot plate.

[0029] Subsequently, on the photoresist film formed on the silicon wafer of nine sheets, the interference prevention film was formed like the example 1, and the photoresist pattern was formed by still more nearly same actuation.

[0030] And when the graph which plotted dimension fluctuation of 0.45-micrometer line pattern on the axis of ordinate, plotted photoresist thickness on the axis of abscissa, and was obtained about the relation of the line pattern dimension of 0.45 micrometers and photoresist thickness which were formed with the same light exposure on the silicon wafer of nine sheets, respectively was shown in drawing 3 , the maximum of dimension fluctuation was about 0.07 micrometers.

[0031] When the photoresist pattern was formed by the same actuation as an example 2 except not using the interference prevention film formation coating liquid used in the example of comparison 2 example 2, it investigated about the relation between the line pattern dimension of 0.45 micrometers, and photoresist thickness similarly and the graph was shown in drawing 4 , the maximum of dimension fluctuation was about 0.17 micrometers.

[0032] After replacing with the interference prevention film formation coating liquid used in the example 3 example 1 and blending perfluoro caprylic-acid ammonium 4g with 10g of polyvinyl-pyrrolidone water solutions 10% of the weight, Except having used the coating liquid which added pure water and prepared the whole as 100g When the photoresist pattern was formed by the same actuation as an example 1, it investigated about the relation between the line pattern dimension of 0.45 micrometers, and photoresist thickness similarly and the graph was shown in drawing 5 , the maximum of dimension fluctuation was about 0.03 micrometers.

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**DESCRIPTION OF DRAWINGS**

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**[Brief Description of the Drawings]**

[Drawing 1] The graph which shows the relation of the thickness about a photoresist and the dimension fluctuation of a line pattern which were obtained in the example 1.

[Drawing 2] The graph which shows the relation of the thickness about a photoresist and the dimension fluctuation of a line pattern which were obtained in the example 1 of a comparison.

[Drawing 3] The graph which shows the relation of the thickness about a photoresist and the dimension fluctuation of a line pattern which were obtained in the example 2.

[Drawing 4] The graph which shows the relation of the thickness about a photoresist and the dimension fluctuation of a line pattern which were obtained in the example 2 of a comparison.

[Drawing 5] The graph which shows the relation of the thickness about a photoresist and the dimension fluctuation of a line pattern which were obtained in the example 3.

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